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Charge Motion Effects in Ionic Clusters

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Abstract

In ionic clusters the polarization depends on the dynamics of charge delocalization. The polarization follows the charge motion when the characteristic time of motion is much longer than the polarization time (~~adi~~abatic polarization). For the opposite case (diabatic polarization), the polarization is determined by an average field. These two kinds of polarization are considered for the ionic clusters Xe_2^+R and $\text{benzene}^+\text{R}$ ($\text{R}=\text{He}, \text{Ne}, \text{Ar}$).

1. Introduction

Ionic atoms and molecules or neutral molecules in excited ionic states can form clusters by attracting neutral closed-shell atoms or molecules. If the ionization potential of the attracted particles is high enough, they will remain neutral inside the cluster. As examples of such clusters we can mention Ar_3^+Ar_n [1-4], aromatic cations with rare gas atoms [5-7], Cl^-Xe_2^+ , or $\text{Cl}^-\text{Xe}^+\text{Xe}_n$ in a rare gas matrix [8,9]. These clusters are kept together mainly by polarization forces.

In simple model calculations the energy of an ionic cluster is presented as a sum of repulsive, dispersive and polarization components. Whereas the repulsive and dispersive components can be considered in the pairwise approach, the polarization energy depends significantly on the cluster geometry and the charge distribution. The last point is of importance for the case of a molecular ionic core of a cluster where the charge is delocalized between some number of atoms. The charge delocalization in a positive ionic cluster core (molecule) can be described as a motion of a positive hole with some characteristic time of the hole "jump" between adjacent atoms. This time is of the order of \hbar/E , where E is the coupling energy responsible for charge delocalization. Since neutral atoms and/or molecules also need some time to be polarized, the interactions between them and the delocalized charge is influenced by dynamical effects. When the polarization time is much smaller than the characteristic time of the hole motion (adiabatic polarization), then the polarization will follow the hole motion and the polarization energy will become an average of the polarization energies of all hole locations. Thus in the case of one neutral atom polarized by an ionic molecule, the adiabatic polarization in the point dipole approximation is

$$U_a = -\frac{\alpha}{2} \sum_i a_i^2 F_i^2 \quad (1)$$

where α is the neutral atom polarizability, a_i^2 is the hole population at the i -th atom, and F_i is the field generated by a hole located at i -th atom. For the opposite case, where the polarization time is much larger than the characteristic time of hole motion (diabatic polarization), the neutral atom will be polarized by an average field,

$$U_d = -\frac{\alpha}{2} \left(\sum_i a_i^2 \vec{F}_i \right)^2 \quad (2)$$

As an example of a system (unrealistic, unfortunately) which demonstrates a dramatic difference between two kinds of polarizations, we can mention an ionic ring with a neutral atom at the ring center. For the adiabatic case the polarization energy is $-\alpha F_i^2/2$ (any i), whereas for the diabatic case it is zero.

The aim of this work is to present the polarization energy for the general case of arbitrary relation between the polarization time and the characteristic time of the hole motion. The dynamical effects of the hole motion on the polarization energy will be described below in the terms of the correlation between the hole location and the polarized-atom electrons.

2. Polarization Energy

Let us consider a cluster consisting of a positively-charged molecular ion M and a neutral atom A polarized by the molecular ion. The positively-charged hole of the isolated molecular ion is described by the wave function

$$\phi_M^{(0)}(r_M) = \sum_i a_i x_i(r_M) , \quad (3)$$

where x_i is the atomic orbital of the hole located at the i -th atom of the molecular ion M. In the zero overlap of atomic orbitals (ZOA) approximation,

$$\langle x_i x_j \rangle = \delta_{ij} , \quad \sum_i a_i^2 = 1 , \quad (4)$$

the energy of the molecular ion M is

$$E_M^{(0)} = \sum_i H_i - 2 \sum_i \sum_{j>i} a_i a_j h_{ij} , \quad (5)$$

where H_i is the energy of diabatic state with located at the i -th atom hole and h_{ij} is the interatomic exchange energy. For the sake of simplicity the neutral atom is assumed to be of S-symmetry, and the wave function of the polarized atom is described as the superposition of S- and P-states:

$$\phi_A^{(0)}(r_A) = b_s S(r_A) + \sum_{k=1}^3 b_k P_k(r_A) , \quad k = x, y, z \quad (6)$$

$$b_s^2 + \sum_{k=1}^3 b_k^2 = 1 . \quad (6')$$

It is assumed that the polarization is weak, $|b_k| \ll b_s$.

We shall present the wave function of the M-A cluster in a form which takes into account the correlation between the hole location and the neutral atom state:

$$\phi(r_M r_A) = \sum_i x_i(r_M) [C_{s,i} S(r_A) + \sum_{k=1}^3 C_{k,i} P_k(r_A)] . \quad (7)$$

We have assumed that the polarization is weak so that the charge (hole) distribution in M is not affected by the polarized atom A:

$$|C_{k,i}| \ll C_{s,i} , \quad C_{s,i}^2 + \sum_{k=1}^3 C_{k,i}^2 = a_i^2 , \quad C_{s,i} = a_i (1 - \frac{1}{2a_i^2} \sum_{k=1}^3 C_{k,i}^2) . \quad (8)$$

Taking into account these relations in the wave function (7), one obtains

$$\phi(r_M r_A) = \sum_i x_i(r_M) [a_i (1 - \frac{1}{2a_i^2} \sum_{k=1}^3 C_{k,i}^2) S(r_A) + \sum_{k=1}^3 C_{k,i} P_k(r_A)] . \quad (9)$$

In the ZOAO approximation this wave function provides the energy expression

$$E = E_M^{(0)} + E_A^{(0)} + E_{MA}^{(0)} + U_{MA} , \quad (10)$$

where $E_M^{(0)}$ and $E_A^{(0)}$ are the energies of the separated molecular ion M and neutral atom A, respectively, $E_{MA}^{(0)}$ is the energy of interaction between the molecular ion and non-polarized atom A, and U is the polarization component of the M-A interaction,

$$\begin{aligned}
 U_{MA} = & \sum_i (\epsilon + \sum_{j \neq i} \frac{a_j}{a_i} h_{ij}) \sum_{k=1}^3 C_{k,i}^2 - \sum_i \sum_{j \neq i} h_{ij} \sum_{k=1}^3 C_{k,i} C_{k,j} \\
 & - 2 \sum_i a_i \sum_{k=1}^3 W_{k,i} C_{k,i} .
 \end{aligned} \tag{11}$$

In Eq. (11) ϵ is the atomic S \rightarrow P excitation energy, and $W_{k,i}$ is the $k = x, y, z$ component of the interaction between the located at the i -th atom charge and the polarized atom. In the point dipole approximation [Eqs. (1)-(2)] the ion and the atom polarized by it are supposed to not overlap with one another. The neglect of overlap leads to the unphysical divergence of $W_{k,i}$ at small separations. In order to prevent this divergency, a damping function γ is introduced into the polarization energy expression [4,7,10],

$$W_{k,i} = \sqrt{\gamma_i} F_{k,i} \mu . \tag{12}$$

where $F_{k,i}$ is the $k=x, y, z$ component of the field generated at the center of the atom A by the hole charge located at the i -th atom of the molecular ion M, and μ is the transition dipole moment,

$$\mu = e \langle P_x S_x \rangle = e \langle P_y S_y \rangle = e \langle P_z S_z \rangle . \tag{13}$$

In the two-state atomic model applied here [Eq. (6)], the transition dipole moment can be expressed by the atom polarizability α as

$$\mu = \sqrt{\alpha \epsilon / 2} . \tag{13'}$$

The damping function γ is taken from Ref. 4 as

$$\gamma(r) = \left[1 + \left[\frac{\rho_i + \rho_A}{r} \right]^{12} \right]^{-1/3}, \quad (14)$$

where r is the separation between the ion i and the atom A , and ρ_i and ρ_A are the atomic radii of the ion and atom, respectively.

Applying the variational principle to the polarization energy (11), we obtain for the coefficients $C_{k,i}$ the system of linear equations

$$\left[\epsilon + \frac{1}{a_i} \sum_{j \neq i} a_i h_{ij} \right] C_{k,i} - \sum_{j \neq i} h_{ij} C_{k,j} = a_i W_{k,i}. \quad (15)$$

Let us consider the solution of Eqs. (15) for two extreme cases, $\epsilon \gg |h_{ij}|$ and $\epsilon \ll |h_{ij}|$. For the first case the coefficients $C_{k,i}$ are

$$C_{k,i} = \frac{a_i}{\epsilon} W_{k,i}. \quad (16)$$

Substituting these coefficients into Eq. (11) and taking into account Eqs. (12) and (13'), one obtains

$$U_{MA} - U_a = -\frac{\alpha}{2} \sum_i a_i^2 \gamma_i \sum_k F_{k,i}^2 = -\frac{\alpha}{2} \sum_i a_i^2 \gamma_i (\vec{F}_i)^2, \quad (17)$$

which is the expression for the adiabatic polarization energy. It differs from expression (1) by the damping functions γ_i only. Physically it is clear that the condition $\epsilon \gg |h_{ij}|$ leads to the adiabatic polarization, since it means that the polarization time is much smaller than the characteristic time

of the hole motion. For the opposite case of diabatic polarization $\epsilon \ll |h_{ij}|$, the polarization time is large so that the neutral atom "feels" the average field. The solution of Eqs. (15) in this case is

$$C_{k,i} = \frac{a_i}{\epsilon} \sum_j a_j^2 W_{k,j} \quad (18)$$

$$U_{MA} - U_d = -\frac{\alpha}{2} \left(\sum_i a_i^2 \sqrt{\gamma_i} \vec{F}_i \right)^2 \quad (19)$$

According to this expression, the average field in the diabatic polarization is weighted by square roots of the damping functions γ_i .

For the particular case of a homonuclear diatomic ion ($i=1,2$), the solution of Eqs. (15) is

$$C_{k,i} = \frac{(\epsilon+h)W_{k,1} + hW_{k,2}}{\sqrt{2} \epsilon(\epsilon+2h)}, \quad C_{k,2} = \frac{(\epsilon+h)W_{k,2} + hW_{k,1}}{\sqrt{2} \epsilon(\epsilon+2h)}, \quad (20)$$

which provides the polarization energy

$$U = -\frac{\alpha}{4(\epsilon+2h)} [\epsilon(\gamma_1 F_1^2 + \gamma_2 F_2^2) + h(\sqrt{\gamma_1} \vec{F}_1 + \sqrt{\gamma_2} \vec{F}_2)^2] \quad (21)$$

The adiabatic ($\epsilon \gg h$) and diabatic ($\epsilon \ll h$) polarization energies are

$$U_a = -\frac{\alpha}{4} [\gamma_1 F_1^2 + \gamma_2 F_2^2] \quad (22)$$

$$U_d = -\frac{\alpha}{8} (\sqrt{\gamma_1} \vec{F}_1 + \sqrt{\gamma_2} \vec{F}_2)^2 \quad (23)$$

The polarization energy (21) becomes equal to the average of U_a and U_d when $h = 0.5\epsilon$. It follows that for the case of a diatomic ion the polarization is adiabatic for $h \ll 0.5\epsilon$ and diabatic for $h \gg 0.5\epsilon$.

Dealing with ionic clusters, we need to know whether to use the adiabatic (17) or diabatic (19) expression. For most of ionic clusters, the adiabatic condition $\epsilon \gg h$ is fulfilled since the exchange term h is usually of the order of 1-2 eV, whereas the excitation energy ϵ of rare gas atoms, for example, is of the order of 10 eV. It is of interest also to know how large the differences are in the adiabatic and diabatic polarization energies. In order to study these differences, we shall consider below the clusters formed by Xe_2^+ ion and rare gas atoms and by an aromatic cation and rare gas atoms.

3. Xe_2^+R (R=He,Ne,Ar) Clusters

In a simple model calculation, the $\text{Xe}_2^+\text{-R}$ potential is presented as a sum of the pairwise van der Waals (vdW) interaction and the R-atom polarization energy. We shall assume that the vdW interaction between the neutral R atom and the charged Xe atom is the same as between two neutral atoms, Xe-R. We shall describe the vdW potential by the L-J(12-6) expression,

$$U_{\text{vdW}} = E \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (24)$$

We have used empirical values [11-14] for the energy E and distance σ . In the expression for the damping function (14) the sum of atomic radii is taken equal to the vdW parameter σ ,

$$\gamma(r) = \left[1 + \left(\frac{\sigma}{r} \right)^{12} \right]^{-1/3} \quad (14')$$

The Xe_2^+R clusters are of T-shaped geometry (Fig. 1). The $\text{Xe}_2^+\text{-R}$ potentials for this geometry are

$$U_d(\rho) = 2U_{\text{vdW}}(r) - C\gamma(r)/r^4 \quad (25)$$

$$U_d(\rho) = 2U_{\text{vdW}}(r) - C\gamma(r)\cos^2\theta/r^4 \quad (26)$$

$$C = \alpha e^2/2, \quad (27)$$

where $r = \rho/\cos\theta$ is the Xe-R separation and ρ is the distance from R atom to the center of Xe_2^+R clusters. Thus, the distances of zero potential ρ_0 and minimum energy ρ_m are smaller in the adiabatic than the diabatic approach by 0.03 Å and 0.03-0.05 Å, respectively (Table 1). The dissociation energy in the adiabatic approach is larger by some 9-13%.

4. Benzene⁺-R Clusters

The ionization potential of benzene-rare gas clusters is red-shifted relative to that of isolated benzene due to the polarization of the rare gas atom by ionized benzene [5]. In model calculations [5-7] the rare gas atom polarization was considered in the averaged field of delocalized benzene⁺ charge, i.e., by the diabatic approach. According to our estimations, however, the adiabatic approach has to be applied in this case. Taking into account that in the benzene-R and benzene⁺-R clusters the rare gas atom R is located on the benzene symmetry axis C_6 , the adiabatic and diabatic polarization energies differ one from another by the coefficient $\cos^2\theta$, like in Eqs. (25)-(26). If to take, for example, the benzene⁺-He cluster, the

minimum energy distance is $\rho_m = 3.0 \text{ \AA}$ [5] which gives $\cos^2 \theta = 0.82$ and the difference between the adiabatic and diabatic polarization energies of some 0.004 eV. In the region of zero potential ($\rho_0 = 2.6 \text{ \AA}$, $r_0 = 3.0 \text{ \AA}$, $\cos^2 \theta = 0.78$) the difference between the two polarization energies is 0.006 eV. As in the case of Xe_2^+R clusters, such a difference in the polarization energy is not crucial for our results, but it is also not negligible, so that in further benzene $^+$ -R clusters calculations it is desirable to use the adiabatic polarization energy.

5. Conclusions

In ionic clusters formed by a polyatomic ionic core and a neutral atom, the atomic polarization is usually faster than the charge motion, so that adiabatic polarization takes place and the polarization energy is determined as an average over the charge locations. For the opposite (diabatic) case, the polarization energy is determined by an average over the field of the charges. As shown for simple ionic clusters, the difference between the adiabatic and diabatic polarization energies is noticeable but not large.

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Table 1. Comparison of the parameters of Xe_2^+R clusters (Fig. 1) obtained with the adiabatic and diabatic polarization energies [Eqs. (25)-(26)]. ρ_0 is the distance of zero potential, ρ_m is the distance of minimum energy, and D_e is the dissociation energy. The distances (σ, ρ_0, ρ_m) are in Å, and the energies (E, D_e) are in eV.

R	σ	E	Ref.	<u>adiabatic</u>			<u>diabatic</u>		
				ρ_0	ρ_m	D_e	ρ_0	ρ_m	D_e
He	3.56	0.00964	12	3.00	3.50	0.0105	3.03	3.55	0.0095
Ne	3.42	0.0258	13	2.87	3.35	0.0138	2.90	3.39	0.0122
Ar	3.80	0.0654	14	3.27	3.80	0.0674	3.30	3.88	0.0620

Figure Caption

Arrangement of atoms in Xe_2^+R cluster.

Fig. 1

